HIGH PRESSURE CO$_2$ ADSORPTION ON ACTIVATED CARBON FIBERS

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INTRODUCTION
Physical adsorption of gases is the most employed technique for the characterization of porous solids [1-3]. N$_2$ adsorption at 77 K is the more used and, usually, has a special status of recommended adsorptive [4]. The advantage of N$_2$ adsorption is that it covers relative pressures from 10^{-8} to 1, what results in adsorption in the whole range of porosity. The main disadvantage of N$_2$ adsorption at 77 K is that when used for the characterization of microporous solids, diffusional problems of the molecules inside the narrow porosity (size < 0.7 nm) occur [5].

CO$_2$ adsorption, either at 273 K or 298 K [5,6], and He adsorption at 4.2 K [7] are two alternatives to N$_2$ adsorption for the assessment of the narrow microporosity. He adsorption at 4.2 K has been proposed [7] as a promising method for the accurate determination of the microporosity. However, the experimental conditions used (adsorption at 4.2 K) makes this technique not so available as CO$_2$ adsorption. In the case of CO$_2$ adsorption the high temperature of adsorption used for CO$_2$ results in a large kinetic energy of the molecules that can enter into the narrow porosity. In this way, CO$_2$ adsorption has been proposed as a good complementary technique, not alternative, for the analysis of the porous texture as it could be used to assess the narrow microporosity (size <0.7 nm).

A confirmation of the reliability of the method for essentially microporous materials, makes necessary the comparison of both N$_2$ and CO$_2$ adsorptions at comparable relative pressures where N$_2$ adsorption has not diffusional limitations. This requires the performance of CO$_2$ adsorption at high pressures. This type of comparison of both adsorptives has not been performed in the literature through the use of high pressure adsorption experiments.

According to all this, the objectives of this work are the following: i) to cover the lack of studies on CO$_2$ adsorption at high pressures; ii) to analyze the adsorption of this gas at relative pressures similar to those used with N$_2$; iii) to show the problems of the use of N$_2$ adsorption at 77 K specially at low relative pressures. All these objetives can be summarized in confirming of the validity of CO$_2$ adsorption to characterize microprous carbon materials.

MATERIALS AND METHODS
A series of activated carbon fibers (ACF) obtained from CO$_2$ (series CFC) activation has been used in this study. The mechanical properties and porosity of these materials have been already analyzed [8]. In summary, the samples are essentially microporous, with a negligible volume of mesopores (only mesoporosity of size larger than 7.5 nm is only observed in samples with high burn-off). Samples with burn-off lower than about 40% have a DR (Dubinin Radushkevich) N$_2$ volume lower than the DR CO$_2$ one, what indicates the existence of narrow microporosity where N$_2$ adsorption has diffusional limitations. The ACF with higher burn-off have some amount of supermicroporosity, as reflected by the larger value of the DR N$_2$ volume compared to the DR CO$_2$.

CO$_2$ adsorption isotherms at 298 K and at high pressures have been carried out in a DMT high pressure microbalance

(Sartorius 4406) connected to a computer for data acquisition. The maximum pressure reached is 4 MPa. Additionally, CO_2 adsorption at 298 K and N_2 adsorption at 77 K up to 0.1 MPa have also been performed with an Autosorb-6 and Omnisorp equipments, respectively, to cover lower relative pressures.

RESULTS AND DISCUSSION
High pressure CO_2 adsorption isotherms at 298 K.
Figure 1 shows CO_2 adsorption isotherms obtained for the samples CFC14 and CFC54, plotted versus the relative fugacity. Each isotherm contains the experiment obtained at sub-atmospheric and at high pressures. It is important to note, by its relevance in the content of the paper, that there is a good continuation in both measurements performed up to sub-atmospheric and high pressures in spite of the different experimental systems used. CO_2 adsorption isotherms can be compared with those obtained from N_2 adsorption at 77 K previously described [8]. The evolution of the isotherms with burn-off is similar for both adsorbates. In fact, several common features can be noted from these experiments: i) the adsorption capacity increases with burn-off and ii) as burn-off increases, the knee of the isotherm widens, showing an increase in microporosity distribution. These results indicate that, due to the range of relative fugacities covered in the high pressure CO_2 adsorption isotherms, this molecule also adsorbs in the supermicroporosity (pore size 0.7-2 nm).

Characteristic curves for N_2 and CO_2 adsorptions.
The characteristic curves that are presented in the following discussion have been obtained by applying the DR equation to the different adsorption measurements performed. The characteristic curves obtained for N_2, correspond to the experiments performed with an Omnisorp apparatus that cover relative pressures from 10^{-7} to 1. The affinity coefficient used in this case is 0.33 [9]. The characteristic curves for CO_2 adsorption contain the isotherms obtained up to sub-atmospheric and up to high pressures. The affinity coefficient for CO_2 has been calculated to have coincident characteristic curves for CO_2 and N_2 adsorptions, in those samples where the adsorption of this gas is not kinetically restricted. From this approach, the coefficient affinity calculated for CO_2 is 0.35, value similar to that proposed by Dubinnin [9].

Figures 2 and 3 include two examples of characteristic curves obtained for samples CFC14 and CFC54 (plots of lnV vs $(A/\beta)^2$). These samples cover the different type of porosity found for the ACF studied. Sample CFC14 has a quite narrow porosity and N_2 adsorption has important diffusional problems. The porosity of sample CFC54 is well developed and contains some amount of supermicroporosity.

There are several relevant points that must be emphasized from Figures 2 and 3. In all the cases, the overlapping and continuation of the CO_2 characteristic curves obtained at low and high pressures is very good. For sample CFC14, the characteristic curve for N_2 adsorption remains always below that for CO_2, in agreement with the kinetically restricted adsorption for N_2 in this sample. With increasing the burn-off, the characteristic curve has not a unique slope and deviates upward. This reflects the development of porosity and the widening of the pore size distribution. This is clearly observed in Figure 3 that corresponds to sample CFC54. In this case, the characteristic curve for N_2 adsorption is very similar to the one for CO_2 obtained at high pressures (see the zone between 0-500 $(kJ/mol)^2$ in Figure 3). This indicates that CO_2 also fills the supermicroporosity that exists in this sample.

Finally, the characteristic curves for N_2 adsorption show in

all the samples a large deviation with respect to the one for CO_2 for values of $(A/\beta)^2$ higher than about 300 $(kJ/mol)^2$. In this zone, the volume of N_2 adsorbed by the sample is lower than the volume of CO_2 and decreases with increasing $(A/\beta)^2$. The adsorption potential, $(A/\beta)^2$, at which this deviation finishes depends on the burn-off of the sample. So, with increasing the burn-off, the recovery of the curve happens at higher $(A/\beta)^2$. This deviation, that happens at low relative pressures of N_2 (lower than 10^{-5} for sample CFC54 and lower than 10^{-4} for sample CFC14), shows that N_2 adsorption in the narrow microporosity is influenced by diffusional limitations. These experimental results are important by their relevance in the use of N_2 adsorption for the characterization of the porosity. As a consequence of the diffusional limitations, N_2 adsorption cannot be used to determine the micropore volue of the narrowest porosity, what makes necessary the use of other adsorptive to analyze this range of porosity. Hence, as already proposed [5], N_2 adsorption, complemented with CO_2 adsorption is an adequated procedure to determine the porosity of an activated carbon from the narrowest to the widest.

CONCLUSIONS
The results commented up to now show that CO_2 adsorption up to sub-atmospheric pressures can be used to calculate the volume of the narrow microporosity and that it is a convenient technique to complement the characterization of porosity through N_2 adsorption. CO_2 adsorbs in the super-microporosity when CO_2 pressures of about 4 MPa are used. The adsorption of N_2 at 77K is limited by diffusional problems that happen in the narrow porosity. For this reason, N_2 adsorption cannot be used to characterize this range of porosity that can be estimated by CO_2 adsorption.

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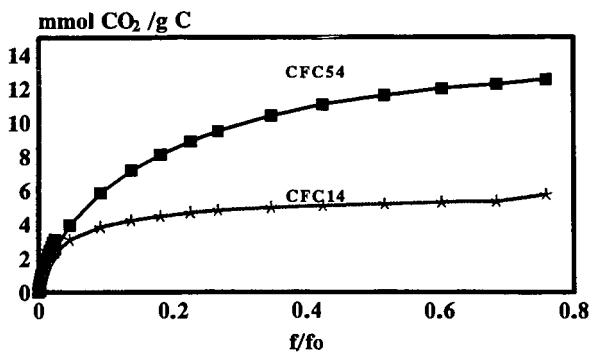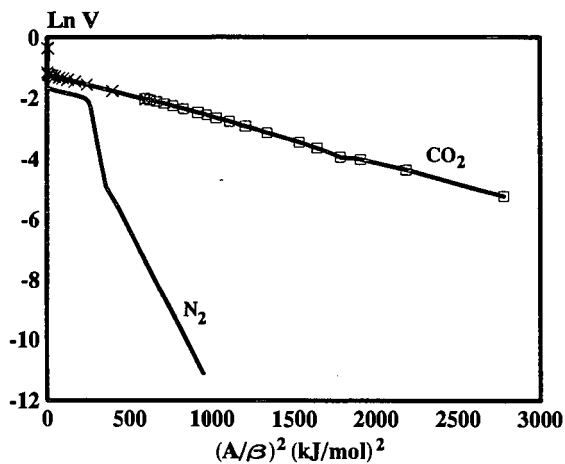
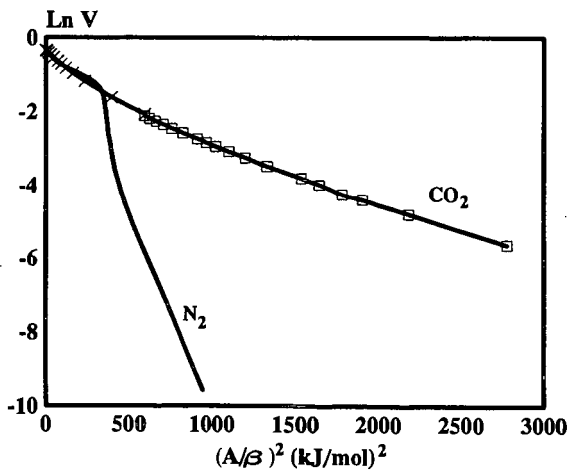**Figure 1.** CO$_2$ adsorption isotherms.

Figure 2. Characteristic curve of sample CFC14

Figure 3. Characteristic curve of sample CFC54

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